High-temperature phase changes in kaolinites.[1]

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Introduction.

NUMEROUS investigations of the effect of heat on minerals of the kaolinite group have established that these minerals are characterized by two major thermal reactions below 1000° C. An intense and abrupt endothermal reaction between 500 and 600° C. has been attributed to the loss of chemically combined water from the kaolinite structure. At about 980° C. these minerals experience an exothermal effect. The intensity and rapidity of this reaction indicate a crystallization process. Certain investigators have ascribed this reaction to the crystallization of gamma alumina (Insley and Ewell, 1935). Comeforo, Fischer, and Bradley (1948), on the other hand, have concluded that it represents crystallization into mullite nuclei of articulated units derived from the original material.

There is disagreement as to the structural state of kaolinite following dehydroxylization and prior to formation of the high-temperature phase, that is, between 600 and 980° C. Insley and Ewell (1935) consider this phase, called metakaolinite, to be an intimate mixture of amorphous SiO_2 and Al_2O_3. Lack of sufficient diffraction data for the anhydride of kaolinite has made it impossible to ascertain directly its structural configuration. Comeforo, Fischer, and Bradley (1948) have shown that the hexagonal morphology of kaolinite persists beyond the point of dehydroxylization, suggesting the persistence of a 'uniquely crystalline' anhydrous phase related structurally to the original material. Recently Brindley (oral communication, 1952) has been able to demonstrate, by means of X-ray diffraction, the existence of a crystalline anhydride phase of nacrite. He concludes that the same regularly constituted, though poorly organized, state is exhibited by metakaolinite.

The purpose of this present study is to present new data pertinent to

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the problems outlined above, to discuss the structural relationships among kaolinite, metakaolinite, and mullite, and to evaluate qualitatively the mechanism by which thermal and crystallographic changes are accomplished in the transformation of one phase to another.

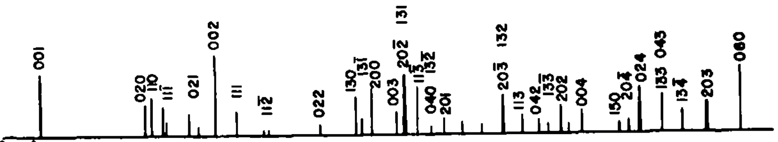
EXPERIMENTAL.

In the course of investigating a number of pure kaolinitic flint-clays, it was noted that the fine fractions ($<$ 2 microns e.s.d.) showed considerable variation in the extent to which their kaolinite component exhibited disordering in the form of random $nb/3$ translations. In the stacking of one kaolinite layer upon the other in a crystallite, glide translations may occur between layers along the *b*-axis, the displacement occurring as integral multiples of one-third the *b*-parameter. Brindley and Robinson (1946) have treated in considerable detail this type of disorder in kaolinites and fireclay minerals.

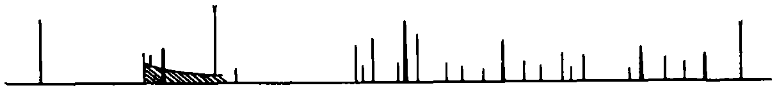
Fig. 1 shows schematically the X-ray powder diffraction data for three kaolinites, representative of twelve samples exhibiting wide variation in stacking. Fig. 1a is a sedimentary kaolin from Dry Branch, Georgia, showing no evidence of $nb/3$ translations. Fig. 1c is a kaolinitic flint-clay from Mt. Savage, Maryland, of the completely disordered type. Lack of all reflections from planes for which $k \neq n3$, and blurring of the (020) reflection is indicative of completely random $nb/3$ translations. Fig. 1b is a kaolinitic flint-clay from Soldier (Hayward), Kentucky, and shows diffraction characteristics common to both the extreme ordered and disordered types, and which can be interpreted as indicating appreciable but not completely random $nb/3$ translations. In twelve samples studied continuous disordering was observed among different samples. The three samples mentioned are sufficient to illustrate the range of types encountered.

X-ray diffraction patterns of powdered materials, oriented aggregates, specimens fired to 600° C., and specimens treated with ethylene glycol, failed to indicate any other clay mineral component in these clays. The Georgia kaolin contained only several per cent. of anatase, the Kentucky flint-clay a trace of quartz and a few per cent. of anatase, and the Maryland flint-clay a little quartz, anatase, and a trace of rutile.

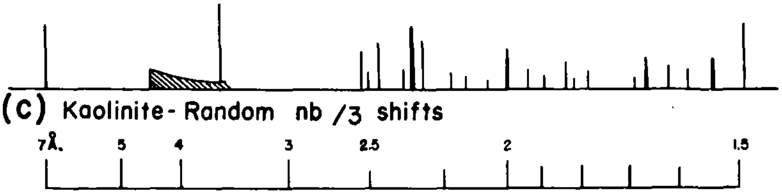
The same samples were subsequently fired to 1000° C., air quenched and subjected to X-ray analysis. (These samples actually represent the residue obtained following differential thermal analysis to 1000° C.) Reproductions of the diffraction patterns are shown in fig. 2. Apart from the small amounts of quartz, anatase, and rutile which are present in the raw materials and remain inert to 1000° C., the Maryland flint-clay fired to gamma alumina; the Kentucky flint-clay exhibited a minor amount of mullite and gamma alumina; and the Georgia kaolin a moderate amount of mullite and gamma alumina. The extent to which mullitization proceeds depends upon the extent of order of the kaolinite. Well-ordered kaolinite develops maximum mullite; completely disordered kaolinite affords no diffraction effects for mullite. Also the crystallinity of the mullite formed is directly related to the crystallinity of the initial kaolinite, as evidenced by the diffuse and generally poor character of diffraction effects for mullite formed from disordered kaolinite as compared to the well-ordered variety.



(a) Kaolinite



(b) Kaolinite- Intermediate



(c) Kaolinite- Random nb /3 shifts

FIG. 1. X-ray powder diagrams of some kaolinite minerals. (*a*) Georgia kaolin; (*b*) Kentucky flint-clay; (*c*) Maryland flint-clay. Indexed according to Pinsker (1950).

It is also of importance to point out that diffraction data for duplicate samples of the same three samples fired to 1000° C. and maintained at that temperature for short periods of time indicate equal development of mullite in spite of initial differences in the nature of the kaolinite. For example, prolonged heating at 1000° C. for one hour was sufficient to show essentially equal development of mullite in the ordered and disordered samples.

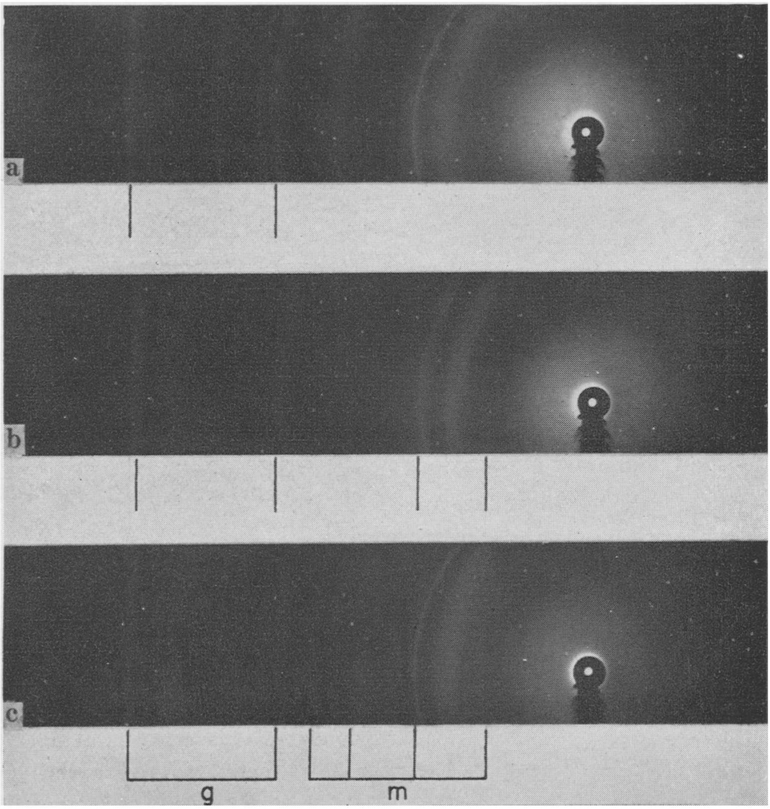


Fig. 2. Powder diffraction patterns of kaolinites fired to 1000° C. (*a*) Maryland flint-clay; (*b*) Kentucky flint-clay; and (*c*) Georgia kaolin. Diagnostic reflections for mullite (m) and gamma alumina (g) indicated. Weaker reflections lost in reproduction.

The same set of samples was subjected to differential thermal analysis between room-temperature and 1000° C. The high-temperature exothermal peaks exhibited no marked variation in intensity and peak temperature indicative of modification of the reaction as a result of disorder of the parent material. Likewise no difference was apparent commensurate with differences in the amount of mullite and gamma alumina shown to be present following completion of the reaction. In addition, all samples showed a slight endothermal effect at about 930° C. The disorder expressed by these kaolinites is actually the result only of variation in the stacking of identical kaolinite units one upon the other, and thermal effects recorded are the result of changes taking place within individual layers. Thus it would not be expected that differences in stacking alone should accomplish marked influence on these reactions.

STRUCTURAL RELATIONS BETWEEN KAOLINITE, METAKAOLINITE, AND MULLITE.

In order to picture the mechanism of the high-temperature transformations experienced by kaolinite, it is necessary to visualize the salient features of the octahedrally co-ordinated levels of kaolinite, metakaolinite, and mullite and the effects imposed upon them by variations in the disorder of kaolinite.

Octahedrally co-ordinated level in kaolinite.

It has been established (Gruner, 1932) that the kaolinite unit of structure is built by the superimposition of tetrahedral Si–O and octahedral Al–O–OH sheets with a ratio of 1:1. There are three possible ways in which these two sheets can be superimposed, by virtue of the fact that only two-thirds of all possible octahedral positions are filled. Fig. 3 illustrates the projection of these three configurations on the basal plane. It will be noted that the only difference in configuration is in the relative positions of the octahedral aluminium ions. In the case of well-ordered kaolinite, only units of the type illustrated by fig. 3a are stacked one above the other oriented with respect to *a*- and *b*-axes. Starting with a well-ordered kaolinite (two or more 3a units directly superimposed), a shift equivalent to $b/3$, of one complete kaolinite unit with respect to another, in effect results in a kaolinite unit of type 3a lying adjacent to a layer of type 3b; a displacement equivalent to $2b/3$ in effect results in a layer of type 3a being contiguous with type 3c. Actually, therefore, a kaolinite exhibiting random $nb/3$ translations exhibits a random distribution in the direction of the *c*-axis of kaolinite units of type 3a, 3b, and 3c. That is to say, there is a random distribution of the Al ion configurations from layer to layer. Such displacements are possible because the OH groups constituting one outer basal surface of kaolinite are repeated at intervals of $b/3$. Random $nb/3$ shifts can likewise be interpreted as random rotations at integral multiples of 120° of one layer with respect to the next. The net effect is the same, but it is more convenient as regards this discussion to consider them from the standpoint of random disposition of the aluminium configurations as described.

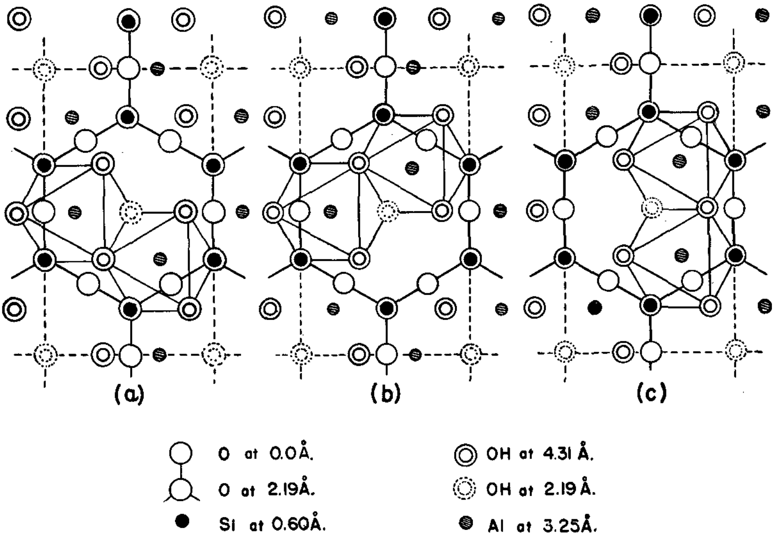


FIG. 3. The structure of the kaolinite layer shown in projection on the basal *ab* plane. Formed by superposition of tetrahedral and octahedral layers (latter co-ordination indicated). (*a*), (*b*), and (*c*) represent alternative methods of superimposing octahedral and tetrahedral layers.

A co-ordination diagram of the octahedral layer of kaolinite is shown in fig. 4a. The corners of each octahedron are occupied by oxygens and/or hydroxyls; the centres by an Al ion. The layer can be visualized as a series of parallel zigzag chains of alumina co-ordination octahedra, each octahedron sharing an edge with three others. In the case of a kaolinite crystallite, composed of numerous kaolinite units, the octahedral portion of one unit will have a counterpart in the contiguous units separated by a tetrahedrally co-ordinated Si–O layer. In well-ordered kaolinite, two or more octahedrally co-ordinated layers, one of which is illustrated by fig. 4a, are situated directly one above the other so that each octahedron, designated by A, has a counterpart in overlying layers exhibiting the same relative orientation in space. Thus octahedral chains are superimposed directly with their axes parallel and each octahedron of one layer is alined in three dimensions with those of the next layer.

Starting with a well-ordered kaolinite, a shift equal to $b/3$ results in the orientation shown in fig. 4b; a displacement of $2b/3$ results in the orientation shown in fig. 4c. Positioning of octahedra of the stationary layer are indicated by A in figs. 4b–4c; A' and A'' represent positioning of octahedra in overlying shifted layers following $b/3$ and $2b/3$ translations respectively. Thus, following a shift equivalent to $b/3$, only one-half of the octahedra in the stationary layer (A) have counterparts in the translated layer (A') which exhibit the same relative orientation; the same is true following a shift of $2b/3$. The net result is that the chains remain oriented parallel, but one-half of the octahedra of each chain are displaced $b/3$ and $2b/3$ respectively. In brief, $nb/3$ translations preserve the general parallel orientation of the larger structural units, the chains of alumina co-ordination octahedra, *but disrupt the three-dimensional alinement of individual octahedra in adjacent kaolinite layers.*

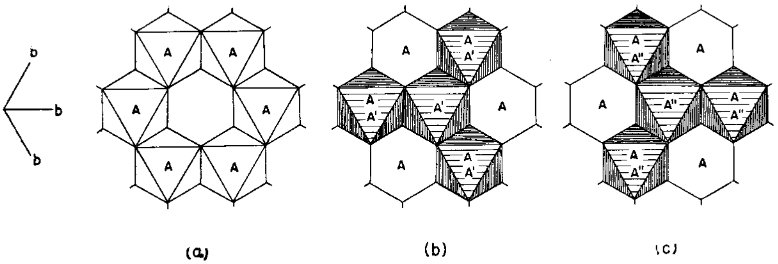


FIG. 4. (*a*) Co-ordination in the octahedral level of kaolinite. Relative position of octahedral units in two adjacent kaolinite layers following (*b*) $b/3$, and (*c*) $2b/3$ translations is shown.

Octahedrally co-ordinated level in metakaolinite.

Diffraction data for the anhydride of kaolinite are insufficient to permit direct determination of the structural make-up of metakaolinite. However, by analogy with the better crystalline anhydride of pyrophyllite-type minerals it is possible to infer something of the structural configuration of the octahedral level of metakaolinite. Bradley and Grim (1951) have shown that dehydroxylization of pyrophyllite-type minerals is accomplished by the rearrangement of octahedral layers with the lifting of the adjacent oxygen layers out of the packed position to positions of direct apposition following abstraction of water. Such a configuration is shown in fig. 5a. The rearrangement which occurs is merely the result of slight rotation of octahedral units as illustrated in fig. 4 to positions

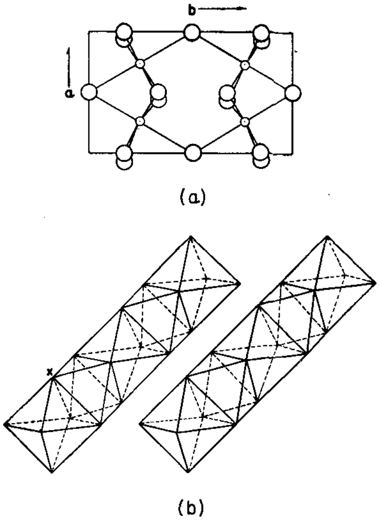


Fig. 5.

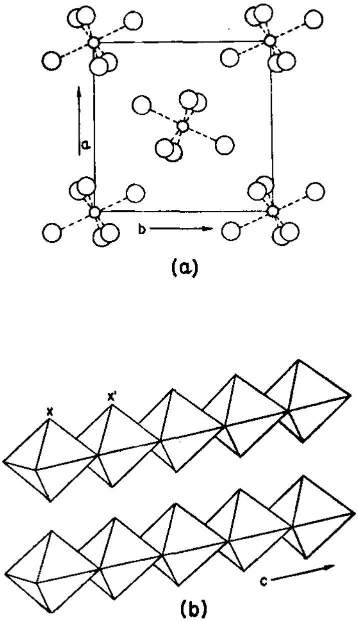


Fig. 6.

Fig. 5. (*a*) Probable arrangement of octahedral level of heptaphyllite type clays (after Bradley and Grim, 1951). (*b*) Octahedral co-ordination chains in metakaolinite.

Fig. 6. (*a*) Unit cell of mullite (after Bragg, 1937); only octahedrally co-ordinated ions shown. (*b*) Mullite-type octahedral co-ordination chains.

where they share pairs of octahedral co-ordination faces instead of edges. Chains of alumina co-ordination octahedra, such as appear in the anhydride of pyrophyllite, are illustrated in fig. 5b. It is important that the parallel orientation of co-ordination chains formed by edge-sharing octahedral units is not disturbed by transition to face-sharing units. Comeforo, Fischer, and Bradley (1948) have suggested that, in the case of metakaolinite also, dehydroxylization results in co-ordinated strings of alumina octahedra of this type, since the distribution of octahedral Al ions in kaolinite is like that of pyrophyllite-type minerals.

It is reasonable to suppose that variations in orientation of octahedral units in kaolinites are carried over into their metakaolinite analogues. Departure from three-dimensional alinement of octahedral units in contiguous layers, afforded by random *nb*/3 translations in kaolinite, is transmitted without change in orientation to metakaolinite also.

Octahedrally co-ordinated levels in mullite.

The structure of mullite has been determined by Taylor (1928). The configuration of the octahedrally co-ordinated portion of mullite is shown schematically in fig. 6a, projected on a plane normal to the *c*-axis. Basically the structure consists of chains of Al–O groups parallel to the *c*-axis, which are seen end on in the projection at the corners and centre of the unit cell (fig. 6a). These chains are formed by each octahedron sharing an edge with a neighbour on each side. Fig. 6b illustrates the co-ordination scheme of octahedra comprising the chain. The chains are linked laterally by Si and Al ions co-ordinated tetrahedrally. The linking ions have been omitted from the projection in order to emphasize the chains of co-ordinated alumina octahedra. In addition to parallel alinement of chains, every Al ion of one chain has a counterpart in the other chains which is coplanar with it with respect to the *ab* plane. In other words, each octahedron is alined in three dimensions with corresponding octahedra in neighbouring chains.

DISCUSSION.

Examination of the *a*- and *b*-parameters of mullite, 7·43 and 7·58 Å. respectively, indicates that more than one unit layer of kaolinite is required for fulfilling the mullite crystallization. The transformation of well-ordered kaolinite to mullite is readily accomplished by the 'condensation' of parallel chains of alumina co-ordination octahedra, each member of which is in three-dimensional alinement, a prerequisite of the mullite structural scheme. Thus well-ordered kaolinite affords maximum opportunity for the formation of mullite, since the proper alinement of octahedral elements, carried over into metakaolinite, is in accord with the requirements imposed by the mullite lattice. In the case of kaolinite exhibiting *nb*/3 translations, the resulting disalinement of octahedral elements, likewise carried over to metakaolinite, would under like conditions be less likely to promote mullitization. Accordingly X-ray diffraction patterns of such materials when fired to 1000° C. fail to show the presence of mullite. Thus the extent to which mullitization proceeds depends upon the magnitude of *nb*/3 shifts, so that a series of kaolinites showing increasing disorder would, upon ignition, form decreasing amounts of mullite. This is in accord with the experimental facts.

The case of halloysite ($2H_2O$) is likewise interesting in this respect. It is considered (Brindley, 1951) that halloysite ($2H_2O$) is built up of contiguous parallel kaolinite layers, but that they are stacked completely randomly with respect to *both a-* and *b*-axes. Halloysite ($2H_2O$) does not form mullite when fired to 1000° C. This is to be expected since disturbance of the parallel alinement of octahedral chains would be at a maximum in this case, and 'condensation' to the mullite structure would be most improbable.

It should now be possible to evaluate qualitatively the energy effects associated with the regrouping of ions in the transformation from kaolinite to metakaolinite to mullite. Likewise a more satisfactory explanation of thermal effects displayed graphically by differential thermal analyses of kaolinite should be forthcoming.

Bradley and Grim (1951), in discussing thermo-chemical generalities as applied to thermal analysis, have pointed out that sharp exothermal effects represent the rapid evolution of hard, dense phases, especially when articulated units present within the structure of the starting material condense without significant rearrangement into crystals of a new phase. Soft, irregularly constituted phases do not evolve detectable energy even in moderately fast precipitation. Accordingly the high-temperature exothermal peak for kaolinite cannot be attributed to the formation of sub-crystalline gamma alumina, found in addition to mullite following ignition to 1000° C. It has been shown that the major change accompanying mullitization involves minor redistribution of octahedrally co-ordinated oxygen ions in the alumina co-ordination chains. Such redistribution results from the transformation of chains composed of octahedral units sharing pairs of co-ordination *faces* (metakaolinite) to chains of *edge-sharing* octahedra (mullite). Pauling (1948) has pointed out that the presence of shared edges and especially shared faces in a co-ordinated structure decreases its stability. The decrease in stability arises from the increased cation–cation Coulomb repulsion. The sharing of an edge between two regular octahedra brings the cations at their centres to a distance from each other only 0·71 times that of octahedrons sharing corners; and the sharing of a face decreases this distance to 0·58 times that for a shared corner. This results in a large increase in crystal energy and decrease in stability of the crystal, especially for highly charged cations. It is, therefore, apparent that transition from the higher energy state of the metakaolinite octahedral chain (face-shared) to the lower energy state of the mullite-type chain (edge-shared) would result in a sudden release of thermal energy and a more stable structure. The transition merely involves a rotation of octahedral elements such that the point of junction of two face-sharing octahedra, indicated by *x* in fig. 5b, is now represented by *x* and *x′* in fig. 6b.

All oxygen ions, except those at the centres of the edges of the unit cell of the anhydride (fig. 5a), are common to both the octahedral layer and a tetrahedral sheet (not shown), each of them constituting an apical oxygen of the overlying Si–O layer. Thus the stability of the octahedral arrangement in the anhydride is derived from and dependent upon the stability of the tetrahedral layer which is a part of it. Accordingly, before the regrouping of octahedral units can occur, sufficient energy must be supplied to render the tetrahedral portion unstable and initiate its breakdown. It is possible that the slight endothermal effect observed at about 930° C., just prior to the major exothermal effect, is associated with the breakdown of the tetrahedral Si–O network.

It is suggested that the high-temperature exothermal effect of kaolinites and halloysites is associated with the transition from face-sharing octahedra of metakaolinite to edge-sharing octahedra of the mullite-type chains. Following such transformation, if, as in the case of well-ordered kaolinite, the proper ion distribution occurs, the mullite crystallization is observed. In the case of disordered kaolinites, following the transition to mullite-type chains, individual octahedra are in improper alinement to result directly in the mullite crystallization. Actually random $nb/3$ shifts do not affect the relative disposition of the oxygen networks of adjacent layers. Change only occurs in the relative distribution of Al ions. Thus following the formation of mullite-type chains, the relative disposition of octahedral units from layer to layer is defined by the positioning of Al ions. The apparent decrease in amount of mullite formed from a sequence of kaolinites exhibiting increasing disorder, may actually be interpreted as a decrease in crystallinity or increase in disorder of comparable amounts of mullite. Accordingly, the exothermal effect must be interpreted as the result of energy involving primarily the rearrangement of the oxygen network to a network *approaching* that of mullite. In the case of disordered kaolinites, the irregular distribution of cations is such that only the oxygen network approximates that of mullite. It was observed that by prolonged heating disordered kaolinite for very short periods of time at 1000° C. it was possible to produce mullite. Sufficient time and energy permit the diffusion of cations into positions in accord with the mullite crystallization.

Thus thermal analysis is most sensitive in revealing the first change which takes place, which represents the rearrangement of packing of the oxygen network. The subsequent reorganization of cations which follows is detected by the development of appropriate diffraction characteristics.

It has been shown (Richardson and Wilde, 1952) that even after heating halloysite at 1000° C. for twenty hours, mullite is not formed. Halloysite must be ignited to 1100° C. before mullite appears. It is evident that at 1000° C. the oxygen network as well as the co-ordinating cations are highly disordered, because of the disordered arrangement of the original halloysite, preventing integration of a mullite lattice. Only $nb/3$ translations result in preservation of the relative configurations of the oxygen networks in successive kaolinite layers, a prerequisite for structural inheritance in the formation of the high-temperature mullite phase. Accordingly, random *a* and *b* translations result in non-parallel alinement of octahedral chains from layer to layer, with ultimate disruption of the oxygen configuration necessary for mullite. Since the energy effects discussed earlier are the results of transformations taking place within individual kaolinite layers, regardless of the manner of superposition of layers, thermal curves for halloysite and kaolinite exhibit the same high-temperature thermal effects.

The presence of gamma alumina along with mullite shows that the thermal effects observed do not necessarily involve the total of all chemical constituents present. A certain amount of alumina is ejected during the recrystallization process. Gamma alumina formed upon ignition to 1000° C. is probably derived largely from incompletely coordinated alumina octahedra occurring at and near the edges of crystallites where the kaolinite structure is incompletely terminated. Thus the flint-clays which are extremely fine-grained develop slightly more gamma alumina than does the Georgia kaolin following ignition to 1000° C. Accordingly, if the high-temperature exothermal effect for kaolinites and halloysite were to be attributed to gamma alumina, the intensity of the reaction should vary directly with the amount of gamma alumina observed. Actually the exactly opposite situation prevails. Rather slight but observable differences in intensity of this reaction are more directly correlative with the mullitization process. Thus gamma alumina appears as an incidental phase with regard to the observed thermal effects.

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